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SOLUTION: After adjusting the concentration of the electrolyte solution obtained by dissolving the solvent containing alcohol, the electrolyte solution is coated on one surface of an electrolyte film into the layered-structure for porous treatment, and an electrolyte solution coated layer is formed into the porous electrolyte having three-dimensional communication holes. Continuously, this electrolyte is laminated on a perfluorosulfonic acid resin film, so that the porous electrolyte film contacts with the resin film. This film is heated at 125° C and pressurized at 50-500 kg/cm² for integral bonding. A three-layered multiple-layered electrolyte film forming with the perfluorosulfonic acid resin film in both sides thereof and the three-dimensional communication holes between them is formed. This multiple-layered electrolyte film holds water in holes parts of the porous electrolyte having the three-dimensional holes for raising the moisture content of the electrolyte film, and increase in the resistance of the electrolyte due to the lowering of the moisture content is restrained.

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CLAIMS

[Claim 1] The double layer electrolyte membrane characterized by at least one electrolyte layer except the electrolyte layer of both sides being the porosity electrolyte which has the hole of three-dimensions free passage nature.

[Claim 2] The manufacture approach of a double layer electrolyte membrane that at least one electrolyte layer except the electrolyte layer of both sides is characterized by being the porosity electrolyte which has the hole of three-dimensions free passage nature by arranging the electrolyte membrane in which the porosity electrolyte layer which has the hole of three-dimensions free passage nature was formed to one [at least] field, to an electrolyte membrane so that a porosity electrolyte layer may touch, and making it into one.

[Claim 3] The solid-state polyelectrolyte mold fuel cell characterized by having claim 1 and a double layer electrolyte membrane according to claim 2.

[Claim 4] The operating method of the solid-state polyelectrolyte mold fuel cell according to claim 3 characterized by supplying a fuel, an oxidizer, or its both by no humidifying.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a solid-state polyelectrolyte mold fuel cell equipped with an electrolyte membrane.

[0002]

[Description of the Prior Art] A solid-state polyelectrolyte mold fuel cell is electrochemistry equipment which supply oxygen to hydrogen and a cathode as an oxidizer, they are made to react to an anode electrochemically as a fuel, and obtains power. It is a gas diffusion electrode, and an anode is joined to one field of an electrolyte membrane, they join a cathode to another field, and an anode and a cathode constitute a gas diffusion electrode-electrolyte membrane zygote. The gas diffusion electrode consisted of a gaseous diffusion layer and a reaction layer, the catalyst bed of an anode and a cathode is equipped with the carbon particle which supported the metal particles or these particles of a platinum metal as a catalyst, and the porosity carbon paper with which a gaseous diffusion layer has water repellence is used.

[0003] The cell which pinches this gas diffusion electrode-electrolyte membrane zygote with the separator of the pair of gas impermeability with which gas supply passage was formed, and serves as a base unit is constituted. The laminating of two or more these cells is carried out, and a solid-state polyelectrolyte mold fuel cell is constituted.

[0004] When a solid-state polyelectrolyte mold fuel cell is operated, with an anode, it is $2H_2 \rightarrow 4H^+ + 4e^-$ With a cathode, it is $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ The electrochemical reaction of $2H_2$ advances.

[0005] a solid-state polyelectrolyte mold fuel cell — it is and the film in which an electrolyte is the film of a macromolecule, for example, it is a kind of the ion-exchange-resin film, and proton conductivity, such as perphloro sulfonic-acid-type-resin film, is shown is used. The proton which these electrolyte membranes showed proton conductivity according to the moisture state, and was generated from hydrogen with the anode is transmitted to a cathode through an electrolyte membrane with some water of hydration, reacts with oxygen, and water generates it. However, by dryness, proton conductivity is not shown, and if the moisture content of an electrolyte membrane decreases, proton conductivity decreases, it has, and as for these electrolyte membranes, membrane resistance increases.

[0006] If a solid-state polyelectrolyte mold fuel cell is operated, the moisture content of the electrolyte membrane by the side of an anode will fall for migration of the water of hydration, and it will become the cause of resistance of an electrolyte membrane of increase. In order to prevent this, the fuel gas supplied to an anode is humidified and supplied to the condition that moisture is included. In a solid-state polyelectrolyte mold fuel cell, since increase of resistance by reduction of the moisture content of an electrolyte membrane increases resistance overvoltage remarkably and causes [of output characteristics] a fall, for a high increase in power, it is important to maintain the high moisture content of an electrolyte membrane.

[0007] In order to maintain the moisture content of an electrolyte membrane, the approach of the water management of a ** sake is proposed in the moisture content of an electrolyte membrane other than the approach of supplying the humidified fuel gas. For example, there is an

approach using the thin electrolyte membrane of thickness. In the cathode side of an electrolyte membrane, moisture content becomes superfluous to an anode side by migration of the water of hydration accompanying the water and the proton shift which are generated by electrode reaction. That is, the inclination of moisture content arises in an electrolyte membrane. At this time, the concentration gradient of the water in an electrolyte membrane serves as driving force, and the back diffusion of electrons of the water by the side of an anode happens from a cathode side. Since a concentration gradient becomes sudden so that an electrolyte membrane is thin, the back diffusion of electrons of water happens mostly, and the contribution to control of a fall of the moisture content by the side of a cathode becomes large.

[0008] Moreover, in order to maintain the moisture content of an electrolyte membrane, there is an approach about the supply approaches of the water to an electrolyte membrane, such as the approach of embedding the fiber which has absorptivity at the approach of contacting an end or some of electrolyte membrane in water, and supplying water or an electrolyte membrane, contacting the end of the fiber in water, and supplying water by the wick. or the inside of the approach of improving water retention by distributing very fine particles, such as titanium oxide, in an electrolyte membrane, or an electrolyte membrane — the very fine particle of platinum — distribution — the approach of improving the moisture content of electrolyte membranes, such as the approach of generating water from the oxygen and hydrogen which penetrate an electrolyte membrane by things, is proposed.

[0009]

[Problem(s) to be Solved by the Invention] However, by the approach of making thickness of an electrolyte membrane thin, if thickness is thin and it carries out, the reinforcement of an electrolyte membrane will decrease. For this reason, in order to maintain the reinforcement which can constitute a solid-state polyelectrolyte mold fuel cell, there is a limitation also in reduction of thickness. It is also required to, heighten the water holding capacity of the electrolyte membrane itself on the other hand, in order to maintain the moisture content of an electrolyte membrane. However, it is difficult to supply water sufficient by the approach using wicks, such as contact in water, and fiber of absorptivity.

[0010] The approach of distributing titanium oxide in an electrolyte membrane is inadequate for improving the water holding capacity of an electrolyte membrane. Moreover, by the approach of distributing platinum in an electrolyte membrane, in order for a production process to become complicated and to use expensive platinum, cost becomes high. Therefore, improving the water retention of an electrolyte membrane and making membrane resistance small for the high increase in power of a solid-state polyelectrolyte mold fuel cell, and the manufacture approach [that the electrolyte membrane is simple and low cost] are required.

[0011]

[Means for Solving the Problem] At least one electrolyte layer except the electrolyte layer of both sides forms the double layer electrolyte membrane which is the porosity electrolyte which has the hole of three-dimensions free passage nature, and improvement in the water nature of an electrolyte membrane is aimed at by making water hold to the hole of this porosity electrolyte layer. By making into an electrolyte membrane and one the electrolyte membrane which formed in the field the porosity electrolyte layer which has the hole of three-dimensions free passage nature at least at one side so that a porosity electrolyte layer may touch, at least one electrolyte layer except the electrolyte layer of both sides offers manufacture ***** of a double layer electrolyte membrane which has the hole of three-dimensions free passage nature and which is a porosity electrolyte layer.

[0012] The solid-state polyelectrolyte mold fuel cell with which at least one electrolyte layer except the electrolyte layer of both sides is equipped with the double layer electrolyte membrane which is the porosity electrolyte which has the hole of three-dimensions free passage nature is constituted. While reducing the resistance overvoltage which aims at improvement in the water nature of an electrolyte membrane, controls and has increase of membrane resistance, and originates in membrane resistance and carrying out a high increase in power of the solid-state polyelectrolyte mold fuel cell, even when it supplies without humidifying a fuel and an oxidizer, the moisture content of an electrolyte membrane is maintained and an output is

stabilized.

[0013]

[Embodiment of the Invention] The manufacture approach of the double layer electrolyte membrane of this invention consists of the following two phases.

[0014] In a phase 1, the porosity electrolyte layer which has the hole of three-dimensions free passage nature is formed in one [at least] field of an electrolyte membrane.

[0015] In a phase 2, the double layer electrolyte membrane of this invention is produced by arranging an electrolyte membrane equipped with the porosity electrolyte layer which has the hole of the produced three-dimensions free passage nature to an electrolyte membrane so that a porous electrolyte layer may touch, and making it into one.

[0016] First, a phase 1 is explained.

[0017] The porosity electrolyte layer which has the hole of three-dimensions free passage nature is producible as follows. That is, after adjusting the concentration of the solution of the electrolyte which dissolved in the solvent containing alcohols, it applies to one [at least] field of an electrolyte membrane in the shape of a layer, and porosity—ization—processes, and the spreading layer of an electrolytic solution is used as the porosity electrolyte which has the hole of three-dimensions free passage nature. Porosity—ized processing is immersed in the organic solvent which has polar groups other than an alcoholic hydroxyl group, and the porosity electrolyte which the electrolyte which is dissolving by this processing solidifies and has the hole of three-dimensions free passage nature is formed.

[0018] Below, an example of the approach of production of a porosity electrolyte layer which has the hole of three-dimensions free passage nature is explained concretely.

[0019] As a solution which dissolved the electrolyte in the solvent containing alcohols, the 5wt% Nafion solution (the U.S. and Aldrich) which is a solution of commercial perphloro sulfonic acid type resin can be used. The Nafion solution of various concentration is prepared by condensing this Nafion solution.

[0020] As an electrolyte membrane, Nafion 112 film (U.S., Du Pont) which is commercial perphloro sulfonic-acid-type-resin film can be used. After boiling this electrolyte membrane with purified water for 1 hour, it saves at the purified water of a room temperature. Take out this swollen electrolyte membrane from ethanol, and ethanol with a membranous excessive front face is wiped off with a paper towel etc. then — for example, . which it is immersed [.] in ethanol, such as ethanol, and makes an electrolyte membrane swell further — After applying to the field of one side at least the Nafion solution which prepared above-mentioned concentration with the means of a spray etc. and forming an electrolyte membrane-electrolytic solution spreading object, as an organic solvent which has polar groups other than an alcoholic hydroxyl group For example, in butyl acetate, it is immersed and the above-mentioned electrolyte membrane-electrolytic solution spreading object is left.

[0021] Then, if an electrolyte membrane-electrolytic solution spreading object is taken out from butyl acetate and it dries at a room temperature, the electrolyte membrane in which the porosity electrolyte layer of an electrolyte membrane which has the hole of three-dimensions free passage nature in the field of one side was formed is producible at least. In addition, Nafion is the trademark of Du Pont.

[0022] Although explained here using the 5wt% Nafion solution which is a solution of commercial perphloro sulfonic acid type resin as a solution which dissolved the electrolyte in the solvent containing alcohols That this invention is not limited to this solution and should just be the solution of perphloro sulfonic acid type resin For example, the solution of other perphloro sulfonic acid type resin, such as deflection myon (trademark of Asahi glass), can be used, and the concentration of an electrolytic solution can be changed into arbitration by approaches, such as dilution or concentration.

[0023] As for electrolytic dilution, carbon numbers, such as a methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, or 2-butanol, can use mixture for four or less alcohol, water, or these. Concentration can remove some solvents of an electrolytic solution by approaches, such as heating and a vacuum drying.

[0024] Although explained using Nafion 112 as an electrolyte membrane, which film may be used

as long as it is the poly membrane which shows proton conductivity according to moisture states, such as electrolyte membranes of a hydrocarbon system, such as electrolyte membranes of a fluorine system, such as other perphloro sulfonic-acid film and perphloro carboxylic-acid film, or a styrene vinylbenzene sulfonic acid. Moreover, the casting film produced from the electrolytic solution can also be used besides the electrolyte membrane marketed by the shape of film. However, in these poly membranes, the fluorine system electrolyte membranes excellent in thermal resistance, such as perphloro sulfonic-acid film and perphloro carboxylic-acid film, are desirable.

[0025] Spreading of the electrolytic solution to an electrolyte membrane has a doctor blade method, screen printing, etc. as approaches other than a spray, and can use a well-known approach conventionally.

[0026] As for the alcohol to which humidity of the electrolyte membrane of a moisture state is carried out, the carbon number other than ethanol can also use four or less methanol, 1-propanol, 2-propanol, 1-butanol, or 2-butanol.

[0027] the carbon number of the chain which the organic solvent which has polar groups other than an alcoholic hydroxyl group is not limited to butyl acetate, and has an alkoxy carbonyl group in intramolecular — the organic solvent of 1-7 — for example Formic acid propyl, formic acid butyl, formic acid isobutyl, ethyl acetate, propyl acetate, Isopropyl acetate, an acetic-acid allyl compound, butyl acetate, isobutyl acetate, pentyl acetate, Isopentyl acetate, methyl propionate, ethyl propionate, propionic-acid propyl, A methyl acrylate, butyl acrylate, isobutyl acrylate, methyl butyrate, Isobutyric-acid methyl, ethyl butylate, isobutyric-acid ethyl, a methyl methacrylate, the carbon number of independent or the chains which have ether linkage in mixture or intramolecular, such as butanoic acid propyl, isobutyric-acid isopropyl, 2-ethoxyethyl acetate, and acetic-acid 2-(2 ethoxy ethoxy) ethyl, — the organic solvent of 3-5 — for example Dipropyl ether, dibutyl ether, ethylene glycol wood ether, the carbon number of independent or the chains which have a carbonyl group in mixture or intramolecular, such as ethylene glycol diethylether, tripropylene glycol monomethyl ether, and a tetrahydrofuran, — the organic solvent of 4-8 — for example the carbon number of independent or the chains which have an amino group in mixture or intramolecular, such as methyl butyl ketone, methyl isobutyl ketone, methyl hexyl ketone, and dipropyl ketone, — the organic solvent of 1-5 — for example the carbon number of independent or the chains which have a carboxyl group in mixture or intramolecular, such as isopropylamine, an isobutyl amine, a TASHARU butylamine, an isopentyl amine, and diethylamine, — the organic solvent of 1-6 — for example Independent or the things which are obtained from mixture or such combination, such as a propionic acid, a valeric acid, a caproic acid, and oenanthalic acid, can be used.

[0028] Thus, an example of drawing (electron microscope photograph) having shown the situation of the front face of a porosity electrolyte layer which has the hole of producing three-dimensions free passage nature is shown in drawing 2. The hole part is open for free passage, and is formed in three dimensions, and the electrolyte part is continuing reticulated and is formed in three dimensions.

[0029] Moreover, drawing 3 is the mimetic diagram having shown the situation of the basic configuration of the front face of a porosity electrolyte layer which has the hole of three-dimensions free passage nature. The path of the electrolyte part of the porosity electrolyte layer in which 4 has the hole of three-dimensions free passage nature for the diameter of opening of the hole part of the porosity electrolyte layer in which 3 has the hole of three-dimensions free passage nature for the hole part of the porosity electrolyte layer in which 2 has the hole of three-dimensions free passage nature for the electrolyte part of the porosity electrolyte layer in which 1 has the hole of three-dimensions free passage nature is shown, respectively.

[0030] Drawing 2 is a porosity electrolyte layer which has the hole of the three-dimensions free passage nature at the time of using a 16wt% Nafion solution, the path of the electrolyte part of the porosity electrolyte layer in which the diameter of opening of the hole part of a porosity electrolyte layer which has the hole of three-dimensions free passage nature has the hole of 0.3-5.0 micrometers and three-dimensions free passage nature is 0.2-1.0 micrometers, and porosity is 70%.

[0031] The path of the range of 0.1–10 micrometers and the frame part of reticulated skeletal structure can be adjusted to the range of 0.1–30 micrometers, and the concentration of the Nafion solution applied to an electrolyte membrane can adjust porosity for the diameter of opening of the mesh part of the reticulated skeletal structure of a porosity electrolyte layer which has the hole of three-dimensions free passage nature to 10 – 90% in the range. The amount of the Nafion solution to apply can adjust the thickness of the porosity electrolyte layer which has the hole of the three-dimensions free passage nature formed in the field of an electrolyte membrane in 1–50 micrometers.

[0032] Below, a phase 2 is explained.

[0033] At least one electrolyte layer except the electrolyte layer of both sides can produce as follows the double layer electrolyte membrane which is the porosity electrolyte which has the hole of three-dimensions free passage nature, for example. That is, it is made an electrolyte membrane and one so that the porosity electrolyte layer of the electrolyte membrane which equipped one [which was produced in the phase 1 / at least] field with the porosity electrolyte layer which has the hole of three-dimensions free passage nature may touch.

[0034] Below, at least one electrolyte layer except the electrolyte layer of both sides explains concretely an example of the approach of production of a double layer electrolyte membrane which has the hole of three-dimensions free passage nature and which is a porosity electrolyte.

[0035] The laminating of the electrolyte equipped with the porosity electrolyte layer which while produced and has the hole of three-dimensions free passage nature in a field in a phase 1 is carried out to Nafion 112 so that a porous electrolyte layer may touch. The heating pressure welding of this layered product is carried out for 3 minutes at 50kg/cm² – 500kg/cm² and 125 degrees C, and it joins to one. Both sides are Nafion 112 film and the double layer electrolyte membrane of this invention which consists of three layers in which the porosity electrolyte which has the hole of three-dimensions free passage nature among these was formed is formed. The mimetic diagram of the double layer electrolyte membrane of this this invention is shown in drawing 1 .

[0036] In this explanation, although the electrolyte membrane equipped with the porosity electrolyte which has the hole of the three-dimensions free passage nature produced in the phase 1 equips only one side with the porosity electrolyte, it can also use that with which both sides are equipped. In this case, the double layer electrolyte membrane of this invention equipped with the porosity electrolyte which has the hole of three-dimensions free passage nature is formed also in the front face which consists of four layers.

[0037] Although explained using Nafion 112 as an electrolyte membrane joined to an electrolyte membrane equipped with the porosity electrolyte which has the hole of the three-dimensions free passage nature produced in the phase 1, which film may be used as long as it is the poly membrane which shows proton conductivity according to moisture states, such as electrolyte membranes of a hydrocarbon system, such as electrolyte membranes of a fluorine system, such as other perphloro sulfonic-acid film and perphloro carboxylic-acid film, or a styrene vinylbenzene sulfonic acid. Moreover, the casting film produced from the electrolytic solution can also be used besides the electrolyte membrane marketed by the shape of film.

[0038] The pressure, temperature, and time amount when carrying out a heating pressure welding of an above-mentioned electrolyte membrane are decided by such balance, and conditions are decided according to a case 50kg/cm² – 500kg/cm² and in 100 degrees C – 175 degrees C.

[0039] Moreover, the double layer electrolyte membrane with which the imperforation electrolyte layer and the porous electrolyte layer had structure at the double three-layer layer electrolyte membrane of produced this invention repeatedly as a laminating is carried out so that a porous electrolyte layer may touch, and it joined to one with a heating pressure welding and the electrolyte equipped with the porosity electrolyte layer which has the hole of three-dimensions free passage nature in one [further] field was shown at drawing 4 can be constituted.

[0040] Thus, by repeating that arbitration carries out count junction of the electrolyte which equipped one field with the porosity electrolyte layer which has the hole of three-dimensions free passage nature, an imperforation electrolyte layer and a porous electrolyte layer can

constitute the double layer electrolyte membrane of this invention which has repetition structure which is the count of arbitration.

[0041]

[Example] Next, the suitable example of this invention is explained with reference to a drawing.

[0042] An example of implementation of the manufacture approach of the double layer electrolyte membrane of [example 1] this invention is explained. Drawing 5 is the float Fig. having shown an example of operation of the production process of the double layer electrolyte membrane of this invention. Manufacture of the double layer electrolyte membrane of this invention consists of six processes, and explains each process concretely using drawing 5.

[0043] The concentration of an electrolytic solution was prepared at the first process. Taking and agitating a commercial 5wt% Nafion solution into a sample bottle, it heated at 60 degrees and the solution was condensed to 16wt(s)%.

[0044] At the second process, the electrolytic casting film was formed from the condensed Nafion solution. Using the doctor blade which adjusted spacing to 0.33mm, the 16wt% Nafion solution was applied to aluminum foil, it dried, and the casting film of Nafion was formed on aluminum foil. When the thickness of this film is measured, it is about 22 micrometers, and let this be an electrolyte membrane A1.

[0045] At the third process, the porosity electrolyte layer which has the hole of three-dimensions free passage nature in an electrolyte membrane A1 was formed. After applying to the electrolyte membrane A1 on the aluminum foil which produced the 16wt% Nafion solution at the second process using the doctor blade which adjusted spacing to 0.16mm and being immersed in butyl acetate for 10 minutes as porosity-ized processing, the porosity electrolyte layer which dries at a room temperature and has the hole of three-dimensions free passage nature on the front face of the electrolyte membrane A1 on aluminum foil was formed. Let this be an electrolyte membrane A2. The thickness of the formed porous electrolyte layer was about 17 micrometers.

[0046] At the fourth process, the electrolyte membrane A2 was joined and the double layer electrolyte membrane was produced. The laminating of the electrolyte membrane A2 of two sheets formed on aluminum foil is carried out so that a porous electrolyte layer may face each other. This layered product was installed in the press fixture, the heating pressure welding was carried out for 3 minutes at 100kg/cm² and 125 degrees C, the electrolyte membrane A2 of two sheets was joined to one, and the double layer electrolyte membrane of this invention in the condition that aluminum foil adhered was formed in both sides.

[0047] At the fifth process, aluminum foil was removed from the produced double layer electrolyte membrane. It is in the condition that aluminum foil has adhered to both sides of the produced double layer electrolyte membrane. This was immersed in the dilute sulfuric acid of 0.5M, aluminum foil was dissolved and removed, and the double layer electrolyte membrane of this invention was obtained. The thickness of the double layer electrolyte membrane of this this invention was about 59 micrometers in the moisture state.

[0048] At the sixth process, it pretreated to the double layer electrolyte membrane of produced this invention. After moving the produced double layer electrolyte membrane to another dilute sulfuric acid of 0.5M and boiling it for 1 hour, processing which washes 5 times with purified water and uses an electrolyte membrane as a proton mold was performed, and it saved in purified water.

[0049] Thus, let the double layer electrolyte membrane of produced this invention be the double layer electrolyte membrane A.

[0050] The solid-state polyelectrolyte mold fuel cell equipped with the double layer electrolyte membrane A by this invention was produced. . which shows the production approach below — the catalyst bed was first formed in both sides of the double layer electrolyte membrane A of this invention as follows. namely, platinum — 30wt(s)% — in addition to [45ml of purified water] 2.6g of supported carbon catalysts, in addition, a platinum support carbon catalyst is distributed to water / 2-propanol mixed solvent, diffusing 2-propanol 45ml gradually subsequently, and it mixes for 30 minutes using a stirrer further. After agitating for 30 minutes after addition in addition gradually, agitating 0.5ml (the Dupont-Mitsui Fluorochemicals make, a PTFE formed

element: 60%) of dispersion solutions of PTFE into this mixture, agitating 17.5ml (made in [Aldrich] the U.S.) of 5wt% Nafion solutions, gradually, in addition, it agitated for 30 more minutes and catalyst dispersion liquid were produced.

[0051] These catalyst dispersion liquid were applied to the circle configuration with a diameter of 3cm to both sides of the double layer electrolyte membrane A with the spray, it dried and the catalyst bed was formed in both sides of the double layer electrolyte membrane A. The catalyst distribution object was applied so that the content of the platinum catalyst of this catalyst bed might become about 0.5 mg/cm².

[0052] The carbon paper which has next the water repellence judged in diameter of 3cm as a gaseous diffusion layer in the double layer electrolyte membrane A in which the catalyst bed was formed to these both sides has been arranged on both sides, it joined to one with the heating pressure welding (for 120kg/cm², 135 degrees C, and 5 minutes), and the gas diffusion electrode-double layer electrolyte membrane zygote A was produced.

[0053] Thus, the produced gas diffusion electrode-double layer electrolyte membrane zygote A was pinched with the metal separator with which the gas supply way was formed, and the solid-state polyelectrolyte mold fuel cell A of this invention was constituted.

[0054] This solid-state polyelectrolyte mold fuel cell was operated on conditions next, and the cell was supplied by the flow rate from which a utilization factor becomes 70% to . fuel gas which measured the current-voltage characteristic using pure hydrogen. The cell was supplied by the flow rate from which a utilization factor becomes 50% in oxidation gas using pure oxygen. The reactant gas of oxygen and hydrogen was supplied with atmospheric pressure, respectively, and humidified neither of the reactant gas. It circulated through the 65-degree C coolant on the cell, and cell temperature was kept constant.

[0055] After purified water washed Nafion 112 film of [example 2] marketing 3 times, and having boiled with the hydrogen peroxide solution of concentration 3% for 1 hour, and having carried out time washing with purified water, and then 0.5M having boiled for dilute-sulfuric-acid 1 hour and permuting by the proton mold, purified water washed 5 times. Let this be an electrolyte membrane B.

[0056] It is the following, and the solid-state polyelectrolyte mold fuel cell equipped with this electrolyte membrane B was made and produced.

[0057] First, the catalyst dispersion liquid prepared in the example 1 with the spray were applied to the circle configuration with a diameter of 3cm to both sides of an electrolyte membrane B, it dried and the catalyst bed was formed in both sides of an electrolyte membrane B. The catalyst distribution object was applied so that the content of the platinum catalyst of this catalyst bed might become about 0.5 mg/cm².

[0058] The carbon paper which has next the water repellence judged in diameter of 3cm as a gaseous diffusion layer in the electrolyte membrane B in which the catalyst bed was formed to these both sides has been arranged on both sides, it joined to one with the heating pressure welding (for 120kg/cm², 135 degrees C, and 5 minutes), and the gas diffusion electrode-electrolyte membrane zygote B was produced.

[0059] Thus, the produced gas diffusion electrode-electrolyte membrane zygote B was pinched with the metal separator with which the gas supply way was formed, and the solid-state polyelectrolyte mold fuel cell B of this invention was constituted.

[0060] This solid-state polyelectrolyte mold fuel cell B was operated on the same conditions as an example 1, and the current-voltage characteristic was measured.

[0061] The current-voltage characteristic of the solid-state polyelectrolyte mold fuel cell produced in the examples 1 and 2 is shown in drawing 6 . The solid-state polyelectrolyte mold fuel cell A equipped with the double layer electrolyte membrane A of this invention has cell voltage higher than the solid-state polyelectrolyte mold fuel cell B equipped with the usual electrolyte membrane so that clearly from drawing 6 . In spite of operating reactant gas by non-humidified operation, a solid-state polyelectrolyte mold fuel cell equipped with the double layer electrolyte membrane of this invention is high power.

[0062] The internal resistance in the condition that these solid-state polyelectrolyte mold fuel cells are operating was measured using the internal resistance meter (TSURUGA MODEL 3562).

The relation of current-internal resistance is shown in drawing 7 . If, as for the solid-state polyelectrolyte mold fuel cell B, a current increases, internal resistance will also increase, but even if, as for the solid-state polyelectrolyte mold fuel cell A, a current increases, most increases of internal resistance are not seen. Water is held at the hole part of the porosity electrolyte with which the double layer electrolyte membrane with which the solid-state polyelectrolyte mold fuel cell A is equipped has the hole of three-dimensions free passage nature, and the moisture content of an electrolyte membrane becomes high. For this reason, it is thought that increase of resistance of the electrolyte membrane resulting from the fall of the moisture content of an electrolyte membrane is controlled.

[0063] That is, even if it supplies without the resistance overvoltage resulting from increase of the membrane resistance of an electrolyte membrane becoming small and humidifying the gas of a fuel or an oxidizer, since the water retention of an electrolyte membrane will improve, if the double layer electrolyte membrane of this invention is used, the solid-state polyelectrolyte mold fuel cell which operates to stability can be offered.

[0064]

[Effect of the Invention] When the double layer electrolyte membrane of this invention forms the porosity electrolyte which has the hole of three-dimensions free passage nature, electrolytic water retention increases. For this reason, when this double layer electrolyte membrane is used for a solid-state polyelectrolyte mold fuel cell, even if it operates with non-humidified reactant gas, increase of the membrane resistance resulting from reduction of the moisture content of an electrolyte membrane can be controlled, it has and a high increase in power by reduction of the resistance overvoltage of a solid-state polyelectrolyte mold fuel cell can be attained.

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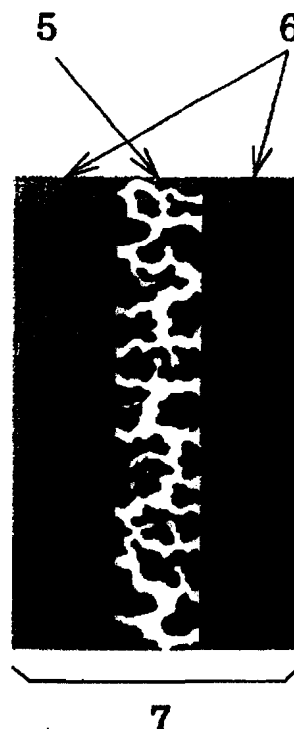
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(54) 【発明の名称】 電解質膜およびその製法とそれを用いた固体高分子電解質型燃料電池ならびにその運転方法

(57) 【要約】

【課題】 保水性が高く、膜抵抗が小さい電解質膜を提供する。

【解決手段】 電解質膜に三次元連通性の孔を有する多孔質電解質層を設ける。



【特許請求の範囲】

【請求項1】 両側の電解質層を除く少なくともひとつの電解質層が三次元連通性の孔を有する多孔質電解質であることを特徴とする複層電解質膜。

【請求項2】 少なくとも一方の面に三次元連通性の孔を有する多孔質電解質層を形成した電解質膜を多孔質電解質層が接するように電解質膜に配置して一体にすることにより、両側の電解質層を除く少なくともひとつの電解質層が三次元連通性の孔を有する多孔質電解質であることを特徴とする複層電解質膜の製造方法。

【請求項3】 請求項1および請求項2記載の複層電解質膜を備えることを特徴とする固体高分子電解質型燃料電池。

【請求項4】 燃料もしくは酸化剤あるいはその両方が無加湿で供給されることを特徴とする請求項3記載の固体高分子電解質型燃料電池の運転方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、電解質膜を備える固体高分子電解質型燃料電池に関するものである。

【0002】

【従来の技術】固体高分子電解質型燃料電池は、アノードに燃料として例えば水素およびカソードに酸化剤として例えば酸素とを供給して電気化学的に反応させて、電力を得る電気化学装置である。アノードおよびカソードはガス拡散電極であり、電解質膜の一方の面にアノードを、もう一方の面にカソードを接合してガス拡散電極-電解質膜接合体を構成する。ガス拡散電極はガス拡散層と反応層とからなり、アノードおよびカソードの触媒層は白金族金属の金属粒子あるいはこれらの粒子を担持したカーボン粒子などを触媒として備えており、ガス拡散層は撥水性を有する多孔質なカーボンペーパーなどが用いられる。

【0003】このガス拡散電極-電解質膜接合体をガス供給流路が形成されたガス不透過性の一对のセパレータで挟持して基本単位となる単電池を構成する。この単電池を複数個積層して固体高分子電解質型燃料電池を構成する。

【0004】固体高分子電解質型燃料電池を作動させるとアノードでは、



カソードでは、



の電気化学反応が進行する。

【0005】固体高分子電解質型燃料電池において電解質は高分子の膜であり、たとえばイオン交換樹脂膜の一種でありパーフロスルホン酸樹脂膜などのプロトン伝導性を示す膜が用いられる。これらの電解質膜は含水状態でプロトン導電性を示し、アノードで水素から生成したプロトンは数個の水和水をともなって電解質膜を介して

カソードに伝達されて酸素と反応して水が生成する。しかし、これらの電解質膜は乾燥状態ではプロトン導電性を示さず、また電解質膜の含水量が低減するとプロトン伝導性が低減し、もって膜抵抗が増大する。

【0006】固体高分子電解質型燃料電池を作動すると、水和水の移動のためにアノード側の電解質膜の含水量が低下し、電解質膜の抵抗の増大の原因となる。これを防止するために、アノードに供給される燃料ガスは水分を含む状態に加湿して供給される。固体高分子電解質型燃料電池において、電解質膜の含水量の低減による抵抗の増大は抵抗過電圧を著しく増大させて出力特性の低下の原因となるので、高出力化のためには電解質膜の高い含水量を保つことが重要である。

【0007】電解質膜の含水量を保つために、加湿した燃料ガスを供給する方法の他に、電解質膜の含水量を保つための水管理の方法が提案されている。たとえば、膜厚の薄い電解質膜を用いる方法がある。電解質膜のカソード側では、電極反応で生成する水およびプロトン移動にともなう水和水の移動とにより、アノード側に対して含水量が過剰になる。つまり電解質膜中では含水量の勾配が生じる。このとき電解質膜中の水の濃度勾配が駆動力となってカソード側からアノード側への水の逆拡散が起こる。電解質膜が薄いほど濃度勾配が急になるので水の逆拡散は多く起こり、カソード側の含水量の低下の抑制への寄与が大きくなる。

【0008】また、電解質膜の含水量を保つために、電解質膜の一端あるいは一部を水と接触させて水を供給する方法や電解質膜に吸水性を有する繊維等を埋め込んでその繊維の一端を水に接触させてウィックにより水を供給する方法など電解質膜への水の供給方法に関する方法がある。あるいは、電解質膜中に酸化チタンなどの微細粒子を分散することにより保水性を向上する方法や電解質膜中に白金の微細粒子を分散することにより電解質膜を透過してくる酸素と水素とから水を生成する方法など電解質膜の含水量を向上する方法が提案されている。

【0009】

【発明が解決しようとする課題】しかしながら、電解質膜の膜厚を薄くする方法では、膜厚の薄くすれば電解質膜の強度が低減する。このために固体高分子電解質型燃料電池を構成しうる強度を維持するために膜厚の低減にも限界がある。一方、電解質膜の含水量を保つためには、電解質膜自体の保水力を高めることも必要である。しかし、水との接触や吸水性の繊維などのウィックを用いた方法では、十分な水を供給することは困難である。

【0010】電解質膜中に酸化チタンを分散させる方法では、電解質膜の保水力を向上するには不十分である。また、電解質膜中に白金を分散させる方法では、製造工程が煩雑になり、また高価な白金を使用するためにコストが高くなる。したがって、固体高分子電解質型燃料電池の高出力化のために、電解質膜の保水性を向上して膜

抵抗を小さくすること、およびその電解質膜の簡易で低コストな製造方法が必要である。

【0011】

【課題を解決するための手段】両側の電解質層を除く少なくともひとつの電解質層が三次元連通性の孔を有する多孔質電解質である複層電解質膜を形成して、この多孔質電解質層の孔に水を保持させることにより電解質膜の含水性の向上を図る。少なくとも一方に面に三次元連通性の孔を有する多孔質電解質層を形成した電解質膜を多孔質電解質層が接するように電解質膜と一体にすることにより、両側の電解質層を除く少なくともひとつの電解質層が三次元連通性の孔を有する多孔質電解質層である複層電解質膜の製造方法を提供する。

【0012】両側の電解質層を除く少なくともひとつの電解質層が三次元連通性の孔を有する多孔質電解質である複層電解質膜を備える固体高分子電解質型燃料電池を構成し、電解質膜の含水性の向上を図って膜抵抗の増大を抑制し、もって膜抵抗に起因する抵抗過電圧を低減して固体高分子電解質型燃料電池を高出力化するとともに、燃料や酸化剤を加湿しないで供給した場合でも電解質膜の含水量を保ち出力を安定させる。

【0013】

【発明の実施の形態】本発明の複層電解質膜の製造方法は、つぎの2つの段階からなる。

【0014】段階1では、電解質膜の少なくとも一方の面に三次元連通性の孔を有する多孔質電解質層を形成する。

【0015】段階2では、作製した三次元連通性の孔を有する多孔質電解質層を備える電解質膜を多孔質電解質層が接するように電解質膜に配置して一体にすることにより、本発明の複層電解質膜を作製する。

【0016】はじめに、段階1について説明する。

【0017】三次元連通性の孔を有する多孔質電解質層は、つぎのようにして作製できる。すなわち、アルコール類を含有する溶媒に溶解した電解質の溶液の濃度を調整した後、電解質膜の少なくとも一方の面に層状に塗布して多孔化処理し、電解質の溶液の塗布層を三次元連通性の孔を有する多孔質電解質にする。多孔化処理はアルコール性水酸基以外の極性基を有する有機溶媒に浸漬することであり、この処理により溶解している電解質が固化して三次元連通性の孔を有する多孔質電解質が形成される。

【0018】つぎに、三次元連通性の孔を有する多孔質電解質層の作製の方法の一例を具体的に説明する。

【0019】アルコール類を含有する溶媒に電解質を溶解した溶液として、たとえば市販のパーフロロスルホン酸樹脂の溶液である5wt%ナフィオン溶液(米国、アルドリッチ社)を用いることができる。このナフィオン溶液を濃縮することにより、種々の濃度のナフィオン溶液を調製する。

【0020】電解質膜として、たとえば市販のパーフロロスルホン酸樹脂膜であるナフィオン112膜(米国、デュポン社)を用いることができる。この電解質膜を精製水で1時間煮沸してから室温の精製水に保存する。その後、たとえばエタノールなどのエタノールに浸漬して電解質膜をさらに膨潤させる。この膨潤した電解質膜をエタノールから取り出して膜の表面の余分なエタノールをペーパータオルなどで拭き取り、少なくとも片側の面に上述の濃度を調製したナフィオン溶液をスプレーなどの手段により塗布して電解質膜-電解質溶液塗布体を形成した後、アルコール性水酸基以外の極性基を有する有機溶媒として、たとえば酢酸ブチルに前述の電解質膜-電解質溶液塗布体を浸漬して放置する。

【0021】その後、酢酸ブチルから電解質膜-電解質溶液塗布体を取り出して室温で乾燥すると、電解質膜の少なくとも片側の面に三次元連通性の孔を有する多孔質電解質層を形成した電解質膜が作製できる。なお、ナフィオンはデュポン社の登録商標である。

【0022】ここではアルコール類を含有する溶媒に電解質を溶解した溶液として市販のパーフロロスルホン酸樹脂の溶液である5wt%ナフィオン溶液を用いて説明したが、本発明はこの溶液に限定されるものでなく、パーフロロスルホン酸樹脂の溶液であればよく、たとえばフレミオン(旭ガラスの商標)など他のパーフロロスルホン酸樹脂の溶液を用いることができ、また、電解質の溶液の濃度は希釈あるいは濃縮などの方法により任意に変更することができる。

【0023】電解質の希釈はメタノール、エタノール、1-プロパノール、2-プロパノール、1-ブタノールあるいは2-ブタノールなどの炭素数が4以下のアルコールあるいは水もしくはこれらを混合物を用いることができる。濃縮は加熱や真空乾燥などの方法により電解質溶液の溶媒の一部を除くことができる。

【0024】電解質膜としてナフィオン112を用いて説明したが、他のパーフロロスルホン酸膜、パーフロロカルボン酸膜などフッ素系の電解質膜あるいはスチレンビニルベンゼンスルホン酸など炭化水素系の電解質膜など含水状態でプロトン伝導性を示す高分子膜であれば、いずれの膜を用いても構わない。また、膜状で市販されている電解質膜の他に、電解質の溶液から作製したキャスティング膜を用いることもできる。ただし、これら的高分子膜の中では、耐熱性に優れたパーフロロスルホン酸膜やパーフロロカルボン酸膜などのフッ素系電解質膜が好ましい。

【0025】電解質膜への電解質溶液の塗布は、スプレー以外の方法としてたとえばドクターブレード法、スクリーン印刷法などがあり、従来公知の方法を用いることができる。

【0026】含水状態の電解質膜を湿潤させるアルコールは、エタノールの他に炭素数が4以下のメタノール、

1-プロパノール、2-プロパノール、1-ブタノールあるいは2-ブタノールを用いることもできる。

【0027】アルコール性水酸基以外の極性基を有する有機溶媒は酢酸ブチルに限定されるものでなく、分子内にアルコキシカルボニル基を有する炭素鎖の炭素数が1~7の有機溶媒、たとえば、ギ酸プロピル、ギ酸ブチル、ギ酸イソブチル、酢酸エチル、酢酸プロピル、酢酸イソプロピル、酢酸アリル、酢酸ブチル、酢酸イソブチル、酢酸ペンチル、酢酸イソペンチル、プロピオン酸メチル、プロピオン酸エチル、プロピオン酸プロピル、アクリル酸メチル、アクリル酸ブチル、アクリル酸イソブチル、酪酸メチル、イソ酪酸メチル、酪酸エチル、イソ酪酸エチル、メタクリル酸メチル、酪酸プロピル、イソ酪酸イソプロピル、酢酸2-エトキシエチル、酢酸2-(2-エトキシエトキシ)エチル等の単独若しくは混合物、又は分子内にエーテル結合を有する炭素鎖の炭素数が3~5の有機溶媒、たとえば、ジプロピルエーテル、ジブチルエーテル、エチレングリコールジメチルエーテル、エチレングリコールジエチルエーテル、トリプロピレングリコールモノメチルエーテル、テトラヒドロフラン等の単独若しくは混合物、又は分子内にカルボニル基を有する炭素鎖の炭素数が4~8の有機溶媒、たとえば、メチルブチルケトン、メチルイソブチルケトン、メチルヘキシルケトン、ジプロピルケトン等の単独若しくは混合物、又は分子内にアミノ基を有する炭素鎖の炭素数が1~5の有機溶媒、たとえば、イソプロピルアミン、イソブチルアミン、ターシャールブチルアミン、イソペンチルアミン、ジエチルアミン等の単独若しくは混合物、又は分子内にカルボキシル基を有する炭素鎖の炭素数が1~6の有機溶媒、たとえば、プロピオン酸、吉草酸、カブロン酸、ヘプタン酸等の単独若しくは混合物、又はこれらの組み合わせから得られるものを用いることができる。

【0028】このようにして作製したの三次元連通性の孔を有する多孔質電解質層の表面の様子を示した図(電子顕微鏡写真)の一例を図2に示す。空孔部分は連続しており三次元的に形成されており、電解質部分は網状に連続しており三次元的に形成されている。

【0029】また、図3は、三次元連通性の孔を有する多孔質電解質層の表面の基本構成の様子を示した模式図である。1は三次元連通性の孔を有する多孔質電解質層の電解質部分を、2は三次元連通性の孔を有する多孔質電解質層の空孔部分を、3は三次元連通性の孔を有する多孔質電解質層の空孔部分の開口径を、4は三次元連通性の孔を有する多孔質電解質層の電解質部分の径をそれぞれ示す。

【0030】図2は16wt%ナフィオン溶液を用いた場合の三次元連通性の孔を有する多孔質電解質層であり、三次元連通性の孔を有する多孔質電解質層の空孔部分の開口径は0.3~5.0 μm 、三次元連通性の孔を

有する多孔質電解質層の電解質部分の径は0.2~1.0 μm 、多孔度は70%である。

【0031】電解質膜に塗布するナフィオン溶液の濃度によって、三次元連通性の孔を有する多孔質電解質層の網状骨格構造の網目部分の開口径を0.1~10 μm の範囲、網状骨格構造の骨格部分の径を0.1~30 μm の範囲、多孔度を10~90%に範囲に調整することができる。電解質膜の面に形成する三次元連通性の孔を有する多孔質電解質層の厚みは、塗布するナフィオン溶液の量によって、1~50 μm の範囲で調整することができる。

【0032】つぎに、段階2について説明する。

【0033】両側の電解質層を除く少なくともひとつの電解質層が三次元連通性の孔を有する多孔質電解質である複層電解質膜は、たとえばつぎのようにして作製できる。すなわち、段階1で作製した少なくとも一方の面に三次元連通性の孔を有する多孔質電解質層を備えた電解質膜の多孔質電解質層が接するように電解質膜と一体にする。

【0034】つぎに、両側の電解質層を除く少なくともひとつの電解質層が三次元連通性の孔を有する多孔質電解質である複層電解質膜の作製の方法の一例を具体的に説明する。

【0035】段階1で作製した一方の面に三次元連通性の孔を有する多孔質電解質層を備えた電解質を多孔性電解質層が接するようにナフィオン112に積層する。この積層体をたとえば、50 kg/cm^2 ~500 kg/cm^2 、125℃で3分間、加熱圧接して一体に接合する。両側がナフィオン112膜であり、これらの間に三次元連通性の孔を有する多孔質電解質が形成された3層からなる本発明の複層電解質膜が形成される。この本発明の複層電解質膜の模式図を図1に示す。

【0036】この説明では、段階1で作製した三次元連通性の孔を有する多孔質電解質を備える電解質膜は片側にのみ多孔質電解質を備えているが両面に備えるものを用いることもできる。この場合、4層からなる表面にも三次元連通性の孔を有する多孔質電解質を備える本発明の複層電解質膜が形成される。

【0037】段階1で作製した三次元連通性の孔を有する多孔質電解質を備える電解質膜に接合する電解質膜としてナフィオン112を用いて説明したが、他のパーフロスルホン酸膜、パーフロロカルボン酸膜などフッ素系の電解質膜あるいはスチレンビニルベンゼンスルホン酸など炭化水素系の電解質膜など含水状態でプロトン伝導性を示す高分子膜であれば、いずれの膜を用いても構わない。また、膜状で市販されている電解質膜の他に、電解質の溶液から作製したキャスト膜を用いることもできる。

【0038】上述の電解質膜の加熱圧接するときの圧力、温度および時間は、これらの兼ね合いできまり、場

合に応じて、 $50\text{ kg/cm}^2 \sim 500\text{ kg/cm}^2$ 、 $100^\circ\text{C} \sim 175^\circ\text{C}$ の範囲で条件が決められる。

【0039】また、作製した本発明の3層の複層電解質膜に、さらに一方の面に三次元連通性の孔を有する多孔質電解質層を備えた電解質を多孔性電解質層が接するように積層して加熱圧接により一体に接合し、図4に示すように無孔性の電解質層と多孔性の電解質層とがくり返し構造をした複層電解質膜を構成することができる。

【0040】このように一方の面に三次元連通性の孔を有する多孔質電解質層を備えた電解質を任意の回数接合することを繰り返すことにより、無孔性の電解質層と多孔性の電解質層とが任意の回数のくり返し構造をした本発明の複層電解質膜を構成することができる。

【0041】

【実施例】次に、本発明の好適な実施例を図面を参照して説明する。

【0042】〔実施例1〕本発明の複層電解質膜の製造方法の実施の一例について説明する。図5は、本発明の複層電解質膜の製造工程の実施の一例を示したフロート図である。本発明の複層電解質膜の製造は6工程からなり、図5を用いてそれぞれの工程について具体的に説明する。

【0043】第一の工程では、電解質溶液の濃度を調製した。市販の5wt%ナフィオン溶液をサンプル瓶に取り、撹拌しながら60度に加熱して溶液を16wt%まで濃縮した。

【0044】第二の工程では、濃縮したナフィオン溶液から電解質のキャスト膜を形成した。間隔を0.33mmに調整したドクターブレードを用いて16wt%ナフィオン溶液をアルミ箔に塗布して乾燥し、アルミ箔上にナフィオンのキャスト膜を形成した。この膜の厚みを測定したところ約22 μm であり、これを電解質膜A1とする。

【0045】第三の工程では、電解質膜A1に三次元連通性の孔を有する多孔質電解質層を形成した。間隔を0.16mmに調整したドクターブレードを用いて16wt%ナフィオン溶液を第二の工程で作製したアルミ箔上の電解質膜A1に塗布し、多孔化処理として酢酸ブチルに10分間浸漬した後、室温で乾燥してアルミ箔上の電解質膜A1の表面に三次元連通性の孔を有する多孔質電解質層を形成した。これを電解質膜A2とする。形成した多孔性の電解質層の厚みは、約17 μm であった。

【0046】第四の工程では、電解質膜A2を接合して複層電解質膜を作製した。アルミ箔上に形成した2枚の電解質膜A2を多孔性の電解質層が向き合うように積層する。この積層体をプレス治具に設置し、 100 kg/cm^2 、 125°C で3分間加熱圧接して2枚の電解質膜A2を一体に接合し、両面にアルミ箔が付着した状態の本発明の複層電解質膜を形成した。

【0047】第五の工程では、作製した複層電解質膜が

らアルミ箔を除去した。作製した複層電解質膜の両面にはアルミ箔が付着している状態である。これを0.5Mの希硫酸に浸漬し、アルミ箔を溶解して取り除き、本発明の複層電解質膜を得た。この本発明の複層電解質膜の厚みは、含水状態で約59 μm であった。

【0048】第六の工程では、作製した本発明の複層電解質膜に前処理を施した。作製した複層電解質膜を別の0.5Mの希硫酸に移し替えて1時間煮沸した後、精製水で5回洗浄して電解質膜をプロトン型にする処理を施し、精製水中に保存した。

【0049】このようにして作製した本発明の複層電解質膜を複層電解質膜Aとする。

【0050】本発明による複層電解質膜Aを備える固体高分子電解質型燃料電池を作製した。以下にその作製方法を示す。まず、つぎのようにして本発明の複層電解質膜Aの両面に触媒層を形成した。すなわち、白金を30wt%担持したカーボン触媒2.6gに精製水45ml加え、次いで2-プロパノール45mlを徐々に拡散しながら加えて白金担持カーボン触媒を水/2-プロパノール混合溶媒に分散し、さらに撹拌器を用いて30分間混合する。この混合物にPTFEのディスパージョン溶液（三井デュポンフロケミカル社製、PTFE固形成分：60%）0.5mlを撹拌しながら徐々に加えて添加後30分間撹拌した後、5wt%ナフィオン溶液（米国、アルドリッチ社製）17.5mlを撹拌しながら徐々に加え、さらに30分間撹拌して触媒分散液を作製した。

【0051】スプレーによりこの触媒分散液を直径3cmの円形状に複層電解質膜Aの両面に塗布し、乾燥して複層電解質膜Aの両面に触媒層を形成した。この触媒層の白金触媒の含有量が約0.5mg/cm²になるように触媒分散物を塗布した。

【0052】つぎに、この両面に触媒層を形成した複層電解質膜Aにガス拡散層として直径3cmに裁断した撥水性を有するカーボンペーパーを両側に配置して加熱圧接（ 120 kg/cm^2 、 135°C 、5分間）により一体に接合してガス拡散電極-複層電解質膜接合体Aを作製した。

【0053】このようにして作製したガス拡散電極-複層電解質膜接合体Aをガス供給路が形成された金属製のセパレータで挟持して本発明の固体高分子電解質型燃料電池Aを構成した。

【0054】この固体高分子電解質型燃料電池をつぎに条件で作動させて、電流-電圧特性を測定した。燃料ガスには純水素を用いて、利用率が70%になる流量で電池に供給した。酸化ガスには純酸素を用いて、利用率が50%になる流量で電池に供給した。酸素および水素の反応ガスはそれぞれ大気圧で供給し、いずれの反応ガスも加湿しなかった。電池には65 $^\circ\text{C}$ のクーラントを循環して、電池温度を一定に保った。

【0055】〔実施例2〕市販のナフィオン112膜を

精製水で3回洗浄してから3%濃度の過酸化水素水で1時間煮沸して精製水で回洗浄し、つぎに0.5Mの希硫酸1時間煮沸してプロトン型に置換した後、精製水で5回洗浄した。これを電解質膜Bとする。

【0056】この電解質膜Bを備える固体高分子電解質型燃料電池を以下のようにして作製した。

【0057】はじめに、スプレーにより実施例1で調製した触媒分散液を直径3cmの円形状に電解質膜Bの両面に塗布し、乾燥して電解質膜Bの両面に触媒層を形成した。この触媒層の白金触媒の含有量が約0.5mg/cm²になるように触媒分散物を塗布した。

【0058】つぎに、この両面に触媒層を形成した電解質膜Bにガス拡散層として直径3cmに裁断した撥水性を有するカーボンペーパーを両側に配置して加熱圧接(120kg/cm²、135℃、5分間)により一体に接合してガス拡散電極-電解質膜接合体Bを作製した。

【0059】このようにして作製したガス拡散電極-電解質膜接合体Bをガス供給路が形成された金属製のセパレータで挟持して本発明の固体高分子電解質型燃料電池Bを構成した。

【0060】この固体高分子電解質型燃料電池Bを実施例1と同じ条件で作動させて、電流-電圧特性を測定した。

【0061】実施例1および2で作製した固体高分子電解質型燃料電池の電流-電圧特性を図6に示す。図6から明らかであるように、本発明の複層電解質膜Aを備える固体高分子電解質型燃料電池Aは、通常の電解質膜を備える固体高分子電解質型燃料電池Bより電池電圧が高い。反応ガスを無加湿運転で作動しているにもかかわらず、本発明の複層電解質膜を備える固体高分子電解質型燃料電池は高出力である。

【0062】内部抵抗計(TSURUGA MODEL 3562)を用いて、これらの固体高分子電解質型燃料電池の作動している状態での内部抵抗を測定した。電流-内部抵抗の関係を図7に示す。固体高分子電解質型燃料電池Bは電流が増大すると内部抵抗も増大するが、固体高分子電解質型燃料電池Aは電流が増大しても内部抵抗の増大はほとんどみられない。固体高分子電解質型燃料電池Aが備える複層電解質膜は、三次元連通性の孔を有する多孔質電解質の空孔部分に水が保持されて電解質膜の含水量が高くなる。このために電解質膜の含水量の低下に起因する電解質膜の抵抗の増大が抑制されるものと思われる。

【0063】すなわち、本発明の複層電解質膜を用いると、電解質膜の保水性が向上するので電解質膜の膜抵抗

の増大に起因する抵抗過電圧が小さくなり、かつ燃料や酸化剤のガスを加湿しないで供給しても安定に作動する固体高分子電解質型燃料電池を提供することができる。

【0064】

【発明の効果】本発明の複層電解質膜は、三次元連通性の孔を有する多孔質電解質を形成することにより電解質の保水性が増大する。このために固体高分子電解質型燃料電池にこの複層電解質膜を用いた場合、無加湿の反応ガスで作動しても電解質膜の含水量の低減に起因する膜抵抗の増大を抑制することができ、もって固体高分子電解質型燃料電池の抵抗過電圧の低減による高出力化を達成できる。

【図面の簡単な説明】

【図1】本発明の中間層に三次元連通性の孔を有する多孔質電解質層を備えた複層電解質膜の断面を示す模式図である。

【図2】本発明の三次元連通性の孔を有する多孔質電解質層の表面性状を示す図である。(電子顕微鏡写真)

【図3】本発明の三次元連通性の孔を有する多孔質電解質の単位胞を示す模式図である。

【図4】本発明の無孔性の電解質層と三次元連通性の孔を有する多孔質電解質層とが交互に繰り返す構造を有する複層電解質膜の断面を示す模式図である。

【図5】本発明の中間層に三次元連通性の孔を有する多孔質電解質層を備えた複層電解質膜の作製工程を示す図である。

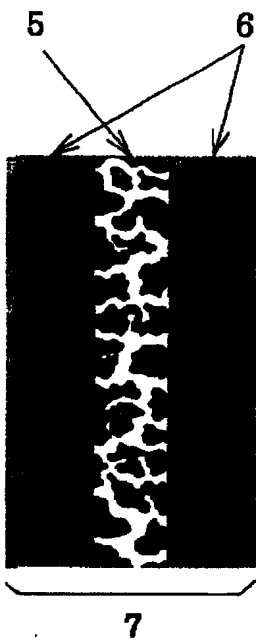
【図6】本発明の複層電解質膜A備えた固体高分子電解質型燃料電池Aおよび公知の電解質膜Bを備えた固体高分子電解質型燃料電池Bとの電流-電圧特性を示す図である。

【図7】本発明の複層電解質膜A備えた固体高分子電解質型燃料電池Aおよび公知の電解質膜Bを備えた固体高分子電解質型燃料電池Bとの電流-内部抵抗の関係を示す図である。

【符号の説明】

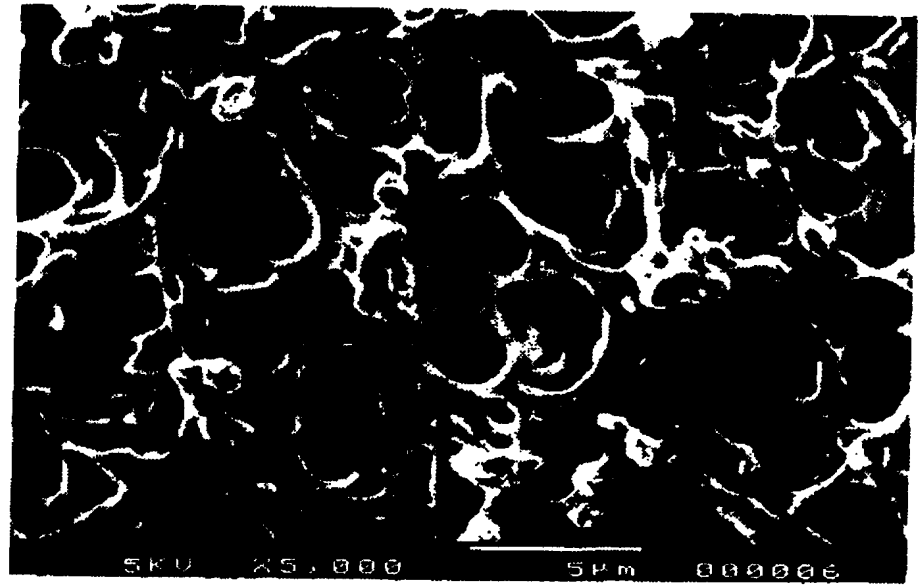
- 1 三次元連通性の孔を有する多孔質電解質層の電解質部分
- 2 三次元連通性の孔を有する多孔質電解質層の空孔部分
- 3 三次元連通性の孔を有する多孔質電解質層の空孔部分の開口径
- 4 三次元連通性の孔を有する多孔質電解質層の電解質部分の径
- 5 三次元連通性の孔を有する多孔質電解質層
- 6 無孔性の電解質層
- 7 本発明の複層電解質膜

【図1】

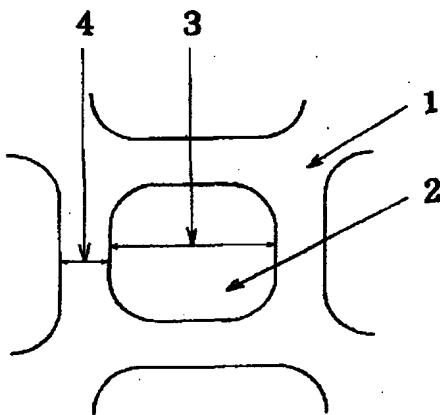


【図2】

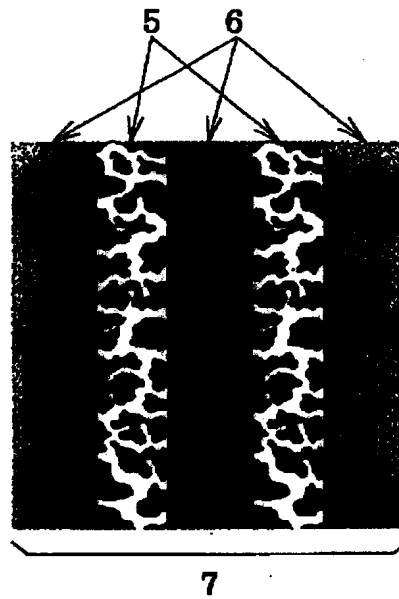
断面代用写真



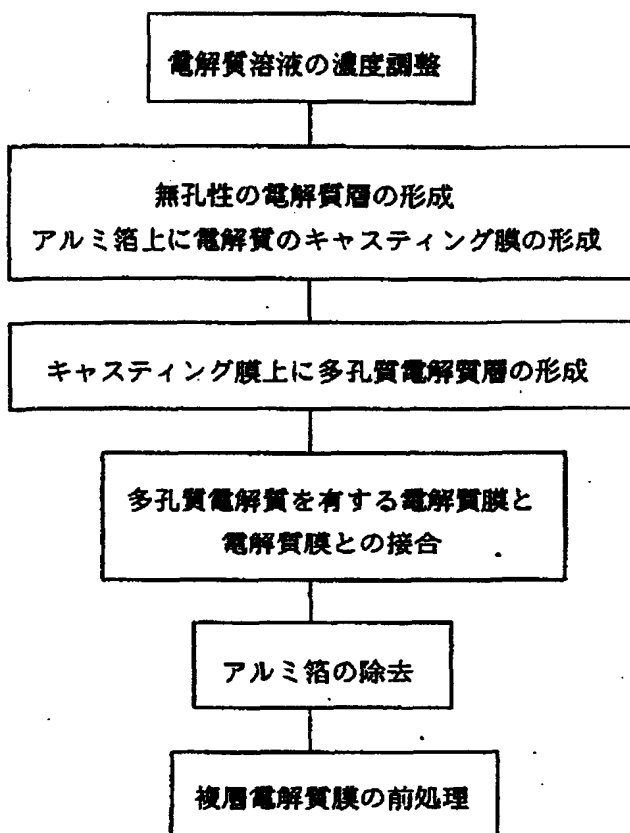
【図3】



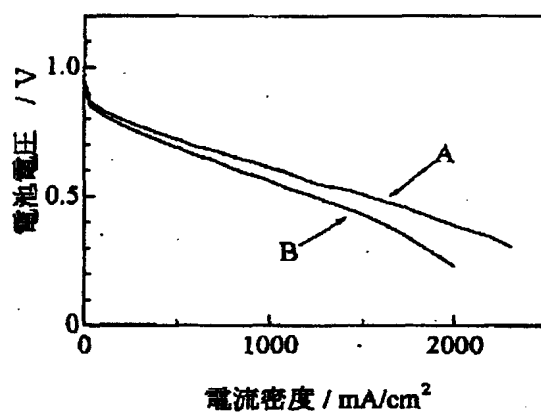
【図4】



【図5】



【図6】



【図7】

